

CO-OXIDATION REACTION ACTIVITY OF Pt CLUSTER CATALYSTS ON $\text{Ti}_{0.9}\text{Mo}_{0.1}\text{O}_2$ SUPPORT

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Received: 15 August 2016; Accepted for publication: 10 November 2016

ABSTRACT

Platinum-based heterogeneous catalysts are critical to many important commercial chemical processes. However, their efficiency is extremely low on a per metal atom basis, because only the surface active-site atoms are used. Catalysts with clusters of atom dispersions are thus highly desirable to increase atom efficiency, but making them is challenging. Here we report the synthesis of a catalyst that consists of isolated clusters of Pt atoms anchored to the surfaces of Molybdenum-doped titanium oxide nanocrystallites. This cluster-atom catalyst has extremely high atom efficiency and shows excellent stability and activity for CO oxidation. The result showed that the highest activity and stability of catalyst with 0.2 wt.% loading of Pt are observed. These could be due to the partially vacant 5d orbitals of the positively charged, high-valent Pt atoms.

Keywords: cluster of Pt atoms, CO oxidation reaction, $\text{Ti}_{0.9}\text{Mo}_{0.1}\text{O}_2$ nanosupport.

1. INTRODUCTION

Supported noble catalysts are the most widely used in industry due to they show high activity and/or selectivity in the large number of different and important chemical reactions [1-4]. Generally, the factors including size, shape, composition, oxidation state, geometry, chemical/physical environments can play an important role in determining nanocrystal reactivity [2]. Many experimental approaches for these nanocatalysts have focused on the fine dispersion of noble metals on a support with a high surface area for the efficient use of catalytically active component [1]. Therefore, in among of these factors, the size of noble metal catalysts is the important consideration for enhancing the catalyst performances [2]. However, the catalytic durability is a huge challenge for the smaller nanometre sized particles or clusters under the effects of high temperature and potential etc. performances. Recently, theoretical and experimental results demonstrated that the sub-nanometre clusters showed better catalytic activity and/or selectivity than nanometre nanoparticles [3, 5, 6]. Low coordination, unsaturated atoms often function as active sites [7], so downsizing the particles or clusters to single atoms is highly desirable for catalytic reactions [1]. One highlighting example is Zhang et al. showed the

single-atomic Pt catalyst on FeO_x support has extremely high atom efficiency and shows that the activity for both CO-oxidation and preferential oxidation of CO in H_2 .

Herein, the atomic Pt clusters including the isolated single atom and cluster-atoms were anchored to the surfaces of $\text{Ti}_{0.9}\text{Mo}_{0.1}\text{O}_2$ nanosupport by a simple hydrothermal method. The Pt cluster catalyst shows very high activity and durability for CO oxidation. The higher activity of the Pt cluster catalyst could be attributed to the partially vacant 5d orbital of positively charged, high-valent Pt atoms. Therefore, the stability of catalyst with low Pt loading can be attributed to the less effects of low CO poisoning.

2. MATERIALS AND METHODS

2.1. Experimental section

2.1.1. Hydrothermal synthesis of atomic Pt clusters on $\text{Ti}_{0.9}\text{Mo}_{0.1}\text{O}_2$ nanosupport

Both sample A (with 0.2 wt.% loading of Pt) and sample B (with 2 wt. % loading of Pt) were prepared by hydrothermal method of an aqueous solution of Chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 0.4 mg for sample A and 4 mg for sample B), Titanium Chloride (TiCl_4 , 28 mM), Molybdenum Chloride (MoCl_5 , 3.1 mM) and Ammonia solution (NH_4OH). In the typical preparation, the pH value of the good mixture including H_2PtCl_6 , TiCl_4 and MoCl_5 precursors in water solvent was adjusted into pH~8 by an ammonia solution at room temperature under the ambient condition. After 15 min for stirring, this mixture was transferred into a Teflon cylinder reactor. Next, a sealed autoclave, which contained the reactor, was heated to 200 °C in an oven and kept at this temperature for 2 hrs. The precipitate of Pt/ $\text{Ti}_{0.9}\text{Mo}_{0.1}\text{O}_2$ samples were collected after the performances such as washing with deionized (DI) water and centrifugations several times. The powders were obtained after drying in a vacuum oven at 80 °C overnight and calcined at 400 °C. Prior to being characterized and tested, the samples were reduced in 10 vol. % H_2/He at 200 °C for 0.5 hrs. The actually Pt loadings in the two samples were determined by inductively coupled plasma spectroscopy were 1.7 wt. % for sample A and 2.2 wt. % for sample B. Noted that the procedure for Pt/ $\text{Ti}_{0.9}\text{Mo}_{0.1}\text{O}_2$ sample synthesis is developed from the procedure for $\text{Ti}_{0.9}\text{Mo}_{0.1}\text{O}_2$ synthesis. Please see the synthesis procedure and characterizations of $\text{Ti}_{0.9}\text{Mo}_{0.1}\text{O}_2$ nanomaterial in our previous work [8, 9].

2.1.2. Characterizations and CO-oxidation activity testing

High resolution-Transition Electron Microscopy (HR-TEM). These measurements were obtained by using a Philips/FEI Tecnai 20G2 S-Twin TEM apparatus. Prior to these measurements, the sample solution was prepared by suspending the catalysts in absolute ethanol solution with ultrasonication. A drop of the specimen was applied onto the carbon-supported copper grid, which was placed in a vacuum oven overnight at 25 °C.

X-ray absorption spectroscopy (XAS) measurements. Pt L_{III}-edge X-ray absorption spectra (EXAFS) were performed on BL17C1 in National Synchrotron Radiation Research Center (NSRRC), Taiwan, operated at ~ 2.2 GeV with injection currents of 200 mA. The Pt foil was used as reference sample and both of Pt foil measured in the transmission mode; both sample A and B were measured in the fluorescence mode with the in-situ system. Before the measurements, the sample A and B were reduced at 200 °C for 30 minutes under a mixing 10 vol. % H_2/He environment (flow rate of 40 mL.min⁻¹). Pt L_{III}-edge measurements data collection

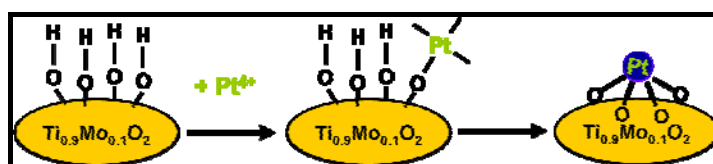
modes, and calculation of errors were all done as per the guidelines set by the International XAFS Society Standards and Criteria Committee [8, 10, 11, 12].

CO-oxidation reaction. The catalytic performance of samples A and B for CO-oxidation reaction was evaluated in a fixed-bed reactor with an in-situ system. Approximated 80 mg of the sample was loaded into a U-shaped quartz reactor, and then was reduced in-situ with 10 vol. % H_2/He at 200 °C for 0.5 hrs. For observing the effect of reaction temperature to CO-conversion percentage, after cooling to 30 °C, the feed gas containing 1 vol. % CO, 1 vol. % O_2 and balance He was allowed to pass through the reactor at a flow of 25 mL.min⁻¹ (corresponding to a space velocity of 18,750 mL.h⁻¹.g_{cat}⁻¹). The effluent gas composition (including before and after CO reaction performances) was analyzed by a gas chromatograph (HP-6000) in the in-situ system. The CO-conversion percentages were calculated by a comparison of CO-peak areas before and after the gas flow pass through the catalyst bed.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Pt atom clusters on $Ti_{0.9}Mo_{0.1}O_2$ nanosupports

Generally, in the reported work, the Pt single atom or sub-nanometre cluster on different supports were synthesized by co-precipitation method and used as hetero-structural catalysts with extremely high activity for CO-oxidation reaction [1]. As a similarity, the Pt atom clusters including single atom and bunch of atoms on $Ti_{0.9}Mo_{0.1}O_2$ nanosupports were synthesized by a simple hydrothermal method. The detail of this synthesis is described in the experimental section. In brief, the Pt ions are adsorbed onto the $Ti_{0.9}Mo_{0.1}O_2$ surface by replacing the proton (hydrogen ions) of -OH groups on this surface (as the Scheme 1), and the Pt single atom/cluster is caught on the oxide support by linking with oxygen. In this research, two levels of Pt⁴⁺ ion concentration are 0.2 weight percent (wt. %) (denoted as sample A, with a Pt/(Ti + Mo) atomic ratio of 1/1591, and a real Pt loading of 0.17 wt. %); 2 wt% (denoted as sample B, with a Pt/(Ti + Mo) atomic ratio of 1/159, and a real Pt loading of 2.2 wt. %). Both of samples were synthesized, characterized, and tested.



Scheme 1. An adsorption mechanism of Pt⁴⁺ ion onto the $Ti_{0.9}Mo_{0.1}O_2$ support surface to form the Pt single atom on the $Ti_{0.9}Mo_{0.1}O_2$ nanosupport.

3.2. Characterizations of Pt/ $Ti_{0.9}Mo_{0.1}O_2$ nanocrystals.

3.2.1. Electron microscopy

The normal TEM machine was used to characterize the samples (see the experimental conditions). Figure 1 shows TEM and Mapping-TEM images of the as-prepared 0.2 wt. % atomic Pt clusters/ $Ti_{0.9}Mo_{0.1}O_2$ nanocrystals. The Pt clusters are observed and circled.

3.2.2. X-ray absorption fine structure studies

The results of electronic diffraction X-ray (EDX)-TEM and X-ray diffraction (XRD) results did not show any Pt-presence in both of these samples due to the insensitivity of XRD measurements to small clusters. However, it was known that the X-ray absorption spectroscopy (XAS) measurements have already used to study the electronic properties of the subnanometre and even single atom of Pt clusters on FeO_x support [1]. Hence, the XAS measurements were also used to examine the electronic properties of these atomic Pt clusters on $\text{Ti}_{0.9}\text{Mo}_{0.1}\text{O}_2$ nanosupports. The XAS results were measured on the freshly reduced Pt catalyst and the K3-weight Fourier transform spectra from EXAFS depicted after the normalizing with Pt mass in the Figure 2. The data show a decreasing trend in the white-line intensities: 0.2 wt. % $\text{Pt}/\text{Ti}_{0.9}\text{Mo}_{0.1}\text{O}_2 > 1$ wt. % $\text{Pt}/\text{Ti}_{0.9}\text{Mo}_{0.1}\text{O}_2 > 2$ wt. % $\text{Pt}/\text{Ti}_{0.9}\text{Mo}_{0.1}\text{O}_2$, which indicates that the Pt clusters in the catalyst A carry positive charges. (a.u. = arbitrary units).

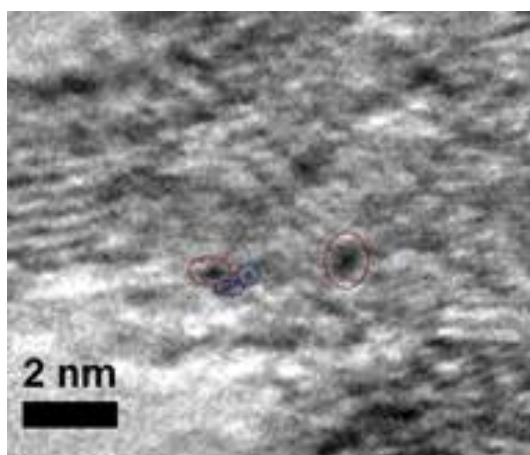


Figure 1. TEM images of 0.2 wt. % atomic Pt clusters/ $\text{Ti}_{0.9}\text{Mo}_{0.1}\text{O}_2$ nanosupports.

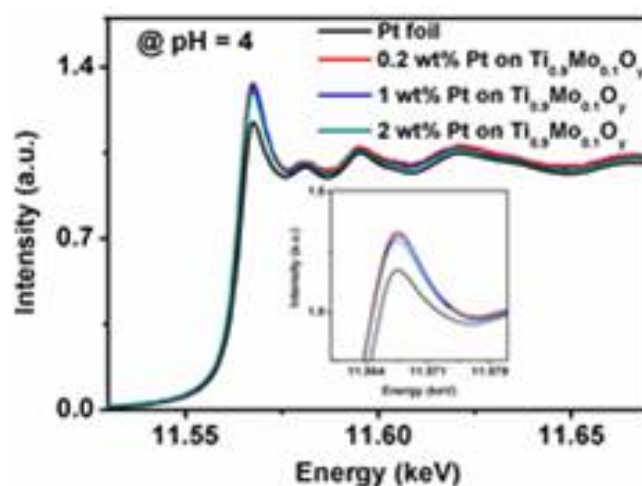


Figure 2. The normalized XANES spectra at the Pt L_{III} edge of sample A and B and Pt foil.

3.2.3. Catalytic performance for CO-oxidation reactions

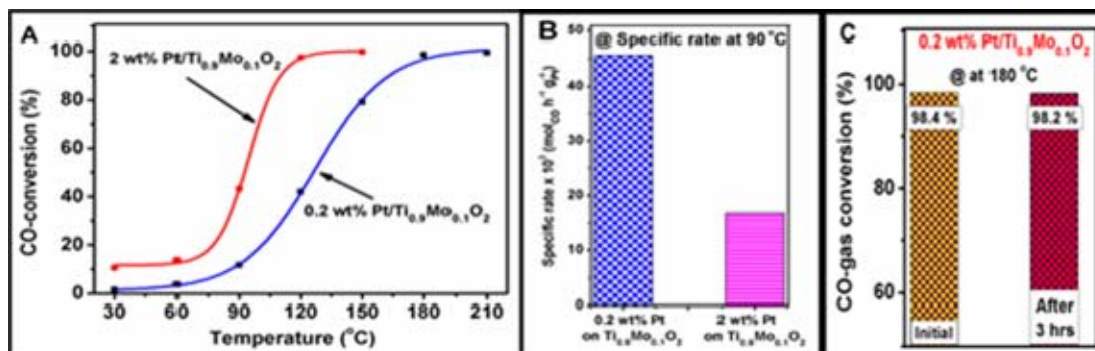


Figure 3. (A) CO-gas conversion, (B) Specific rate at 90 °C of Pt/ $Ti_{0.9}Mo_{0.1}O_2$ catalysts and (C) Catalytic CO-gas oxidation stability of 0.2 wt. % Pt/ $Ti_{0.9}Mo_{0.1}O_2$ catalyst at 180 °C.

The CO-oxidation performances of Pt catalysts on $Ti_{0.9}Mo_{0.1}O_2$ nanosupport are showed in Figure 3. It is noted that the homemade catalysts were pressed and sieved to enhance the stability under the effect of high gas flow rate in the U-reactor. As shown in the Figure 3A, the activated Pt/ $Ti_{0.9}Mo_{0.1}O_2$ catalysts show very high activity for CO-oxidation reaction. The temperature of totally CO-conversion of the sample B (2 wt. % Pt/ $Ti_{0.9}Mo_{0.1}O_2$ catalyst) is lower than that of the sample A (0.2 wt. % Pt/ $Ti_{0.9}Mo_{0.1}O_2$ catalyst). For example, the totally CO-conversion temperature for sample B, and sample A is 120 °C and 180 °C, respectively. Additionally, the differences are observed for the conversion curves of two catalysts toward CO-oxidation. For 2 wt. % Pt/ $Ti_{0.9}Mo_{0.1}O_2$ catalyst, the increasing step of CO-conversion curve is so large. For 0.2 wt. % Pt/ $Ti_{0.9}Mo_{0.1}O_2$ catalyst, however, this observation is opposite. Herein, at the reaction temperature less than 100 °C, these catalysts show the ability for CO-conversion (see Fig. 3A). It is an important issue to applicate this catalyst in the CO contaminant cases with low concentration. Interestingly, at 90 °C, the specific rate of catalyst A is observed to be higher (~2.7-folds) than that of catalyst B (see Fig. 3B and Table 1 more detail). This says that the rate of CO conversion of catalyst A is faster than that of catalyst B.

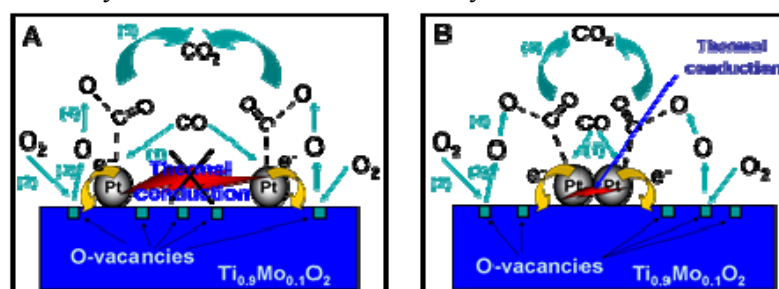


Figure 4. Mechanism of CO-oxidation reaction on $Ti_{0.9}Mo_{0.1}O_2$ nanosupport with (A) single atomic Pt catalyst model and (B) cluster Pt catalyst model. (1) CO adsorption on the Pt sites; (2) O_2 adsorption on oxygen vacancy sites; (3) Oxygen atom generation; (4) the reaction of oxygen atom with CO ads species on the Pt surfaces; and (5) CO_2 desorption from the Pt surfaces.

The Figure 4 could be used to explain these issues. For high CO oxidation activity at less 100 °C are observed for both of catalyst A and B, this can be due to oxygen vacancies are contained on the surface of $Ti_{0.9}Mo_{0.1}O_2$ nanoparticles and positive charge on Pt particle surface. It is well known that the oxidation reaction is strongly supported from oxygen vacancies

[8, 9]. For the large of increasing step of CO-conversion curve, it could be effect of thermal conduction from Pt sites. For the higher activity of 0.2 wt. % Pt/Ti_{0.9}Mo_{0.1}O₂ catalyst, it can be due to higher positive charged on Pt particle surface and high-valent Pt atoms [1].

3.2.4. Stability of 0.2 wt.% Pt/ Ti_{0.9}Mo_{0.1}O₂ catalyst

Table 1. Effect of particle size of Pt catalyst on Ti_{0.9}Mo_{0.1}O₂ nanosupport to CO-oxidation activity.

Sample	Real Pt loading (wt %)	CO-gas oxidation reaction	
		Specific rate (mol _{CO} h ⁻¹ g _{Pt} ⁻¹) At 90 °C	CO conversion Initial-After 3 hrs At 180 °C (%)
Sample A	0.17	4.563	98.4 - 98.2
Sample B	2.20	1.685	-

The stability test of 0.2 wt. % Pt/Ti_{0.9}Mo_{0.1}O₂ catalyst is performed at 180 °C and the result is showed in the Fig. 3C. The stability of catalyst is determined by comparing the CO-conversion coefficients at the initial time and after 3 hrs for CO oxidation reaction. They have not show any effect on the catalytic activity and catalyst A is good stability in the CO oxidation reaction at 180 °C. It is implied that sintering of Pt clusters on nanosupport does not occur during the catalytic reactions.

4. CONCLUSIONS

In summary, the novel catalyst is synthesized and characterized and it consists of clusters of Pt atoms dispersed on a Ti_{0.9}Mo_{0.1}O₂ nanosupport. This catalyst showed extremely high activity for CO oxidation reaction. The chemical reactivity of our positively charged single Pt atoms. The more vacant orbitals of the cluster of Pt atoms, because of the electron transfer from Pt atoms to the Ti_{0.9}Mo_{0.1}O₂ nanosupport surface, are responsible both for the strong binding and stabilization of cluster of Pt atoms and for providing positively charged Pt atoms, which ultimately account for the excellent catalytic activity of the cluster of Pt atoms/Ti_{0.9}Mo_{0.1}O₂ nanosupport catalyst. Although we used CO oxidation to demonstrate the high activity of the cluster of Pt atoms/Ti_{0.9}Mo_{0.1}O₂ nanosupport catalyst, the observed behaviour of cluster of Pt atoms is, nonetheless, not limited to CO oxidation. Moreover, the stabilization of cluster of Pt atoms on practical oxide supports via the charge-transfer mechanism is not limited to the cluster of Pt atoms/Ti_{0.9}Mo_{0.1}O₂ nanosupport system, but can be extended further and made applicable to other precious-metal systems. This catalyst not only proves the concept of cluster-atom heterogeneous catalysis, but also has a great potential to reduce the high cost of commercial noble-metal catalysts in industry.

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